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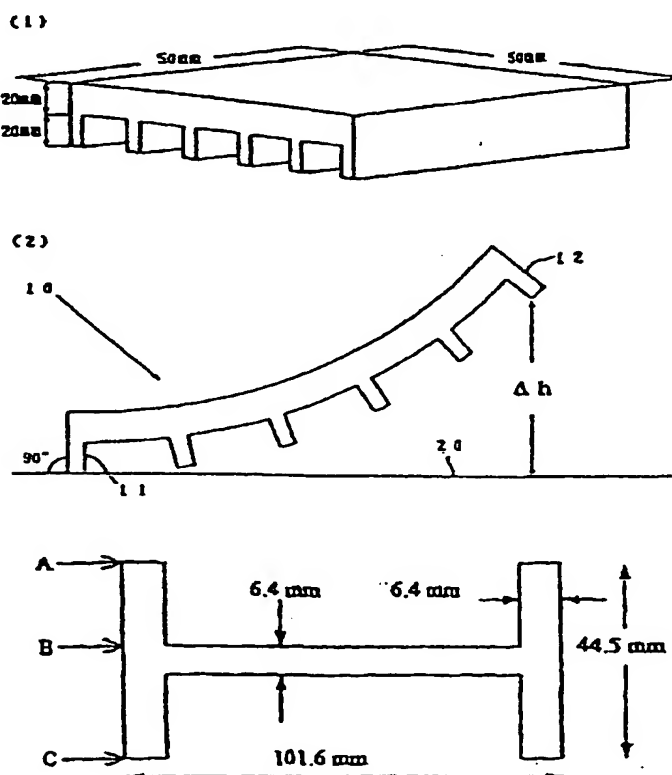
6, 14-15(exs), 16  
mono-oxetane  
iodonium salt  
photoacid gen  
elastomer parts

(54) Title: RESIN COMPOSITION FOR PHOTOFABRICATION OF THREE DIMENSIONAL OBJECTS

(57) Abstract

Photocurable resin composition for photofabrication of three-dimensional objects comprising (A) 5-80 parts by weight of an oxetane compound, (B) 5-80 parts by weight of an epoxy compound, (C) 0,1-10 parts by weight of a photoacid generator, (D) 1-35 parts by weight of elastomer particles with an average particle diameter of 10-700 nm, (E) 0-35 parts by weight of a polyol compound, (F) 0-45 parts by weight of an ethylenically unsaturated monomer, and (G) 0-10 parts by weight of a radical photopolymerization initiator.

42 elast parts



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RESIN COMPOSITION FOR PHOTOFABRICATION OF THREE  
DIMENSIONAL OBJECTS

5

Specification

The present invention relates to a photocurable resin composition for photofabrication of three-dimensional objects which can produce a cured product exhibiting superior photocurability and excellent mechanical strength. More particularly, the present invention relates to a photocurable resin composition for photofabrication of three-dimensional objects which exhibits superior photocurability to various light sources such as a laser and a UV lamp and can produce a cured three-dimensional object exhibiting superior folding endurance, and to a fabricated object produced by photocuring the composition.

In recent years, photofabrication of three-dimensional object consisting of cured resin layers integrally laminated by repeating a step of selectively irradiating a photocurable liquid resin composition has been proposed (see Japanese Patent Application Laid-open Nos. 247515/1985, 35966/1987, 101408/1987, and 24119/1993).

A typical example of such photofabrication is as follows. The surface of a photocurable resin composition in a vessel is selectively irradiated with light from an ultraviolet laser and the like to form a cured resin layer having a specified pattern. The equivalent of one layer of a photocurable resin composition is provided over this cured resin layer and

the liquid surface is selectively irradiated to form a newly cured resin layer integrally laminated over the cured resin layer. This step is repeated a certain number of times using the same or different irradiating patterns to obtain a three-dimensional object consisting of integrally laminated cured resin layers. This photofabrication has attracted considerable attention because a three-dimensional object having a complicated shape can be easily formed in a short period of time.

As the photocurable resin composition used in the photofabrication of three-dimensional objects, the following resin compositions (a) to (c) have been known in the art.

- 15 (a) A resin composition comprising a radically polymerizable organic compound such as urethane (meth)acrylate, oligoester (meth)acrylate, epoxy (meth)acrylate, and photosensitive polyimide (see Japanese Patent Applications Laid-open Nos. 204915/1989, 208305/1990, and 160013/1991).
- 20 (b) A resin composition comprising a cationically polymerizable organic compound such as an epoxy compound, cyclic ether compound, cyclic lactone compound, cyclic acetal compound, cyclic thioether compound, spiro orthoester compound, and vinyl ether compound (see Japanese Patent Application Laid-open No. 213304/1989).
- 25 (c) A resin composition comprising both the radically polymerizable organic compound and the cationically polymerizable organic compound (see Japanese Patent Applications Laid-open Nos. 28261/1990, 75618/1990, and 228413/1994).
- 30

In view of efficiency of photofabrication, the photocurable resin compositions used for the photofabrication preferably possesses low viscosity for immediately forming a smooth liquid surface as well as superior curability to be cured immediately by irradiation. Moreover, the photocurable resin compositions are required to exhibit a small amount of deformation such as warping caused by shrinkage during photocuring.

Three-dimensional objects produced by the photofabrication are used for design models, prototypes for mechanical parts, and the like. Therefore, such three-dimensional objects have to be formed with highly accurate fabrication, specifically, provided with accurate micro-fabrication conforming to the plan, exhibit sufficient mechanical strength under use conditions, and have stable mechanical characteristics which do not change with time.

The three-dimensional objects formed from the photocurable resin composition have been widely used in various fields in satisfying various requirements, for example, fabrication accuracy, hardness, sufficient elasticity, and a small amount of warping caused by cure shrinkage of the liquid resin. It has been thought to be difficult to provide toughness to the fabricated object formed from the photocurable resins because of characteristics of the photocurable resins. However, three-dimensional objects exhibiting toughness, in particular, folding endurance have been demanded accompanying the expansion of the market. A blend of fine particles with the resin composition has been attempted in order to improve

physical properties of the three-dimensional product. Such attempts aim at increasing fabrication accuracy (see Japanese Patent Application Laid-open No. 114733/1991), adjusting light scattering of the  
5 fabricated product (see Japanese Patent Application Laid-open No. 103415/1991), improving toughness of the fabricated object (Japanese Patent Application Laid-open No. 145616/1990), and the like. However, these inventions do not aim at overcoming a shortcoming of  
10 the three-dimensional object of being inferior in repeated folding deformation and have not solved this problem.

The present invention has been achieved based on the above situation.

15 An object of the present invention is to provide a novel photocurable resin composition for the photofabrication of three-dimensional objects.

A second object of the present invention is to provide a photocurable resin composition for  
20 photofabrication of three-dimensional objects capable of producing a three-dimensional object which exhibits superior mechanical strength, high fabrication accuracy, a small amount of warping, and excellent folding endurance, and which is suitably used in  
25 prototypes for mechanical parts and the like.

A third object of the present invention is to provide a three-dimensional object exhibiting superior folding endurance and a small variation in modulus of elasticity with time.

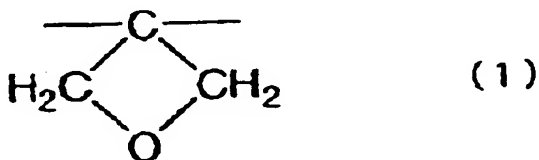
30 Other objects, features and advantages of the invention will hereinafter become more readily apparent from the following description.

First, according to the present invention, the above objects and advantages can be achieved by a photocurable resin composition for photofabrication of three-dimensional objects comprising (A) 5-80 parts by weight of an oxetane compound, (B) 5-80 parts by weight of an epoxy compound, (C) 0,1-10 parts by weight of a photoacid generator, (D) 1-35 parts by weight of elastomer particles with an average particle diameter of 10-700 nm, (E) 0-35 parts by weight of a polyol compound, (F) 0-45 parts by weight of an ethylenically unsaturated monomer, and (G) 0-10 parts by weight of a radical photopolymerization initiator.

According to the present invention, the above objects and advantages can be achieved by a fabricated object produced by photocuring the photocurable resin composition of the present invention.

#### Oxetane compound (A)

An oxetane compound (A) (hereinafter may be called "component (A)") which constitutes the photocurable resin composition for photofabrication of three-dimensional objects of the present invention (hereinafter may be called "resin composition") comprises at least one oxetane ring shown by the following formula (1).

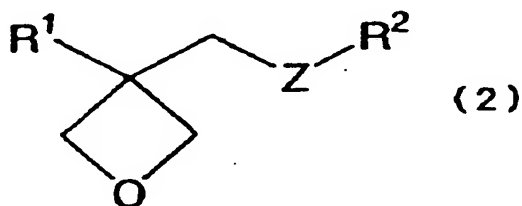


The oxetane compound can be polymerised or

crosslinked by irradiation with light in the presence of a cationically polymerizable photoinitiator.

Oxetane compound (A) comprises at least one oxetane ring. Examples of compound (A) are given below.

5                    Examples of compound (A) having one oxetane ring in the molecule, are shown by the following formula (2):



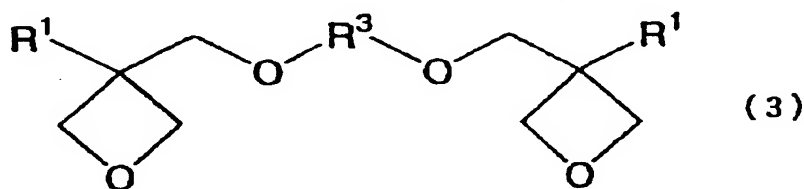
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wherein  $\textcircled{Z}$  represents an oxygen atom or sulphur atom;  $\textcircled{R^1}$  represents a hydrogen atom, fluorine atom, an alkyl group having 1-6 carbon atoms such as a methyl group, ethyl group, propyl group, and butyl group, a fluoroalkyl group having 1-6 carbon atoms such as trifluoromethyl group, perfluoroethyl group, and perfluoropropyl group, an aryl group having 6-18 carbon atoms such as a phenyl group and naphthyl group, a furyl group, or a thienyl group; and  $\textcircled{R^2}$  represents a hydrogen atom, an alkyl group having 1-6 carbon atoms for example a methyl group, ethyl group, propyl group, and butyl group, an alkenyl group having 2-6 carbon atoms for example a 1-propenyl group, 2-propenyl group, 2-methyl-1-propenyl group, 2-methyl-2-propenyl group, 1-butenyl group, 2-butenyl group, and 3-butenyl group, an aryl group having 6-18 carbon atoms for example a phenyl group, naphthyl group, anthranyl group, and phenanthryl group, a substituted or unsubstituted.



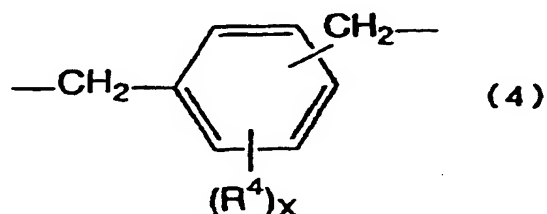
aralkyl group having 7-18 carbon atoms for example a benzyl group, fluorobenzyl group, methoxy benzyl group, phenethyl group, styryl group, cinnamyl group, ethoxybenzyl group, a group having other aromatic rings  
5 for instance an aryloxyalkyl for example a phenoxyethyl group and phenoxyethyl group, an alkylcarbonyl group having 2-6 carbon atoms for example an ethylcarbonyl group, propylcarbonyl group, butylcarbonyl group, an alkoxy carbonyl group having 2-  
10 6 carbon atoms for example an ethoxycarbonyl group, propoxycarbonyl group, butoxycarbonyl group, an N-alkylcarbamoyle group having 2-6 carbon atoms such as an ethylcarbamoyle group, propylcarbamoyle group, butylcarbamoyle group, pentylcarbamoyle group.

15 As examples of compounds having two oxetane rings in the molecule, compounds shown by the following formula (3) can be given:



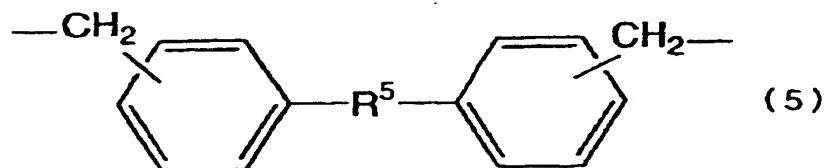
20 wherein R¹ is the same as defined for the above formula (2); R³ represents a linear or branched alkylene group having 1-20 carbon atoms for example an ethylene group, propylene group, and butylene group, a linear or  
25 branched poly(alkyleneoxy) group having 1-120 carbon atoms for example a poly(ethyleneoxy) group and poly(propyleneoxy) group, a linear or branched unsaturated hydrocarbon group for example a propenylene group, methylpropenylene group, and butenylene group, a

carbonyl group, an alkylene group containing a carbonyl group, an alkylene group containing a carboxyl group in the middle of the molecular chain, and an alkylene group containing a carbamoyl group in the middle of the molecular chain; and  $R^3$  may be a polyvalent group selected from groups shown by the following formulas (4), (5), and (6):

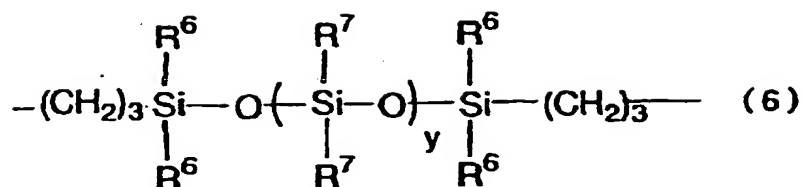


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wherein  $R^4$  represents an alkyl group having 1-4 carbon atoms, an alkoxy group having 1-4 carbon atoms, a halogen atom for example a chlorine atom or bromine atom, a nitro group, cyano group, mercapto group, carboxyl group, or carbamoyl group, and  $x$  is an integer from 1-4;

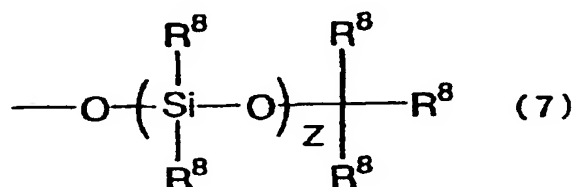


20 wherein  $R^5$  represents an oxygen atom, sulphur atom, methylene group,  $-NH-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-C(CF_3)_2-$ , or  $-C(CH_3)_2-$ ;



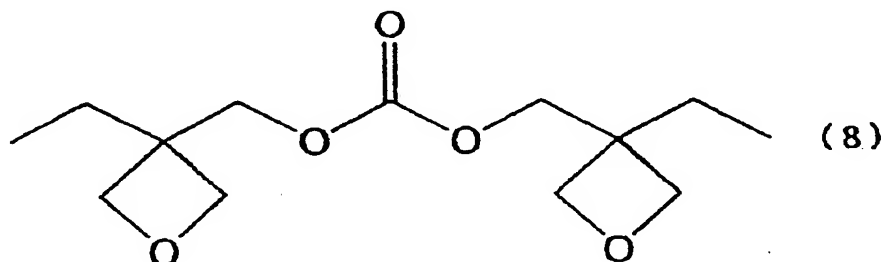
wherein  $\text{R}^6$  represents an alkyl group having 1-4 carbon atoms or an aryl group having 6-18 carbon atoms for example a phenyl group or naphthyl group,  $y$  is an integer from 0-200, and  $\text{R}^7$  represents an alkyl group having 1-4 carbon atoms, an aryl group having 6-18 carbon atoms for example a phenyl group or naphthyl group, or a group shown by the following formula (7):

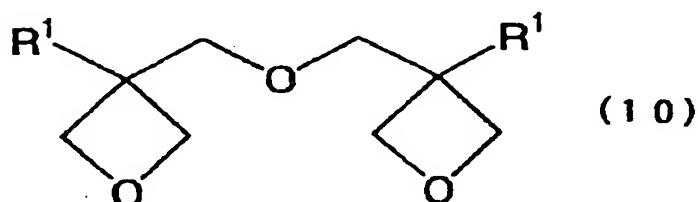
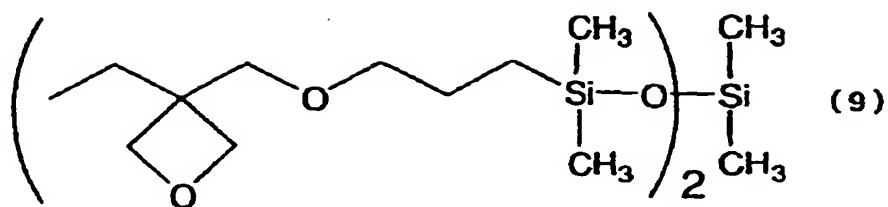
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wherein  $\text{R}^8$  represents an alkyl group having 1-4 carbon atoms or an aryl group having 6-18 carbon atoms for example a phenyl group or naphthyl group, and  $z$  is an integer from 0-100.

As specific examples of the compounds having two oxetane rings in the molecule, compounds shown by the following formulas (8), (9), and (10) can be given.

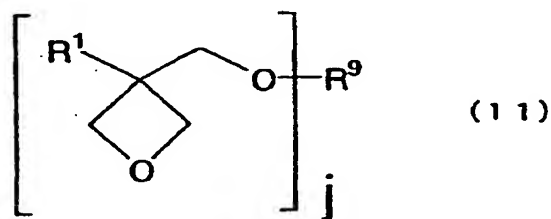




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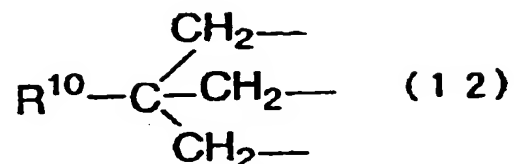
In the formula (10),  $\text{R}^1$  is the same as defined for the above formula (2).

As examples of the compounds having three or more oxetane rings in the molecule, compounds shown by the following formula (11) can be given:

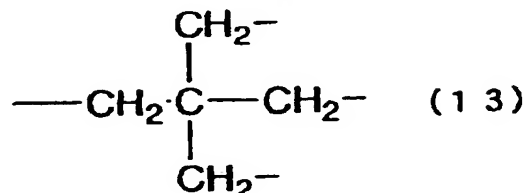


wherein  $\text{R}^1$  is the same as defined for the above formula (2);  $\text{R}^9$  represents an organic group with a valence of 3-10, for example, a branched or linear alkylene group having 1-30 carbon atoms for example groups shown by the following formulas (12)-(14), a branched poly(alkyleneoxy) group for example a group shown by the following formula (15), or a linear or branched polysiloxane containing group shown by the following formula (16) or (17),;  $j$  is an integer from 3-10 which

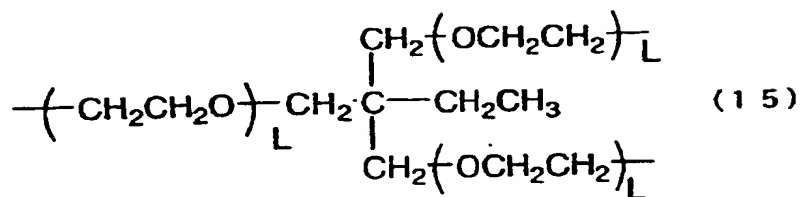
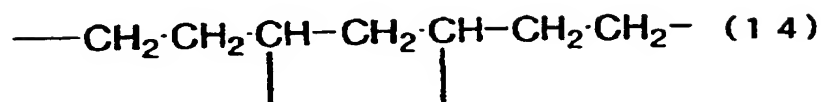
is equal to the valence of  $R^9$ :



- 5 wherein  $R^{10}$  represents an alkyl group having 1-6 carbon atoms:

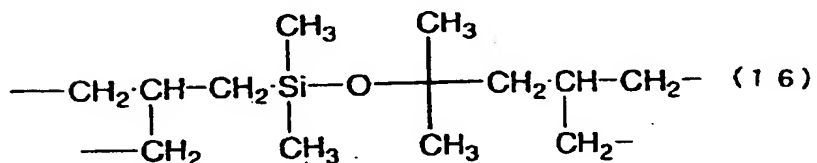


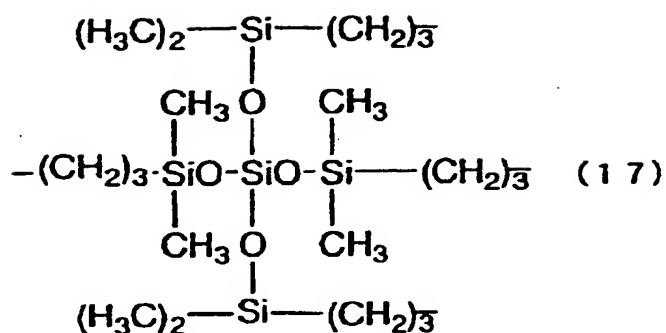
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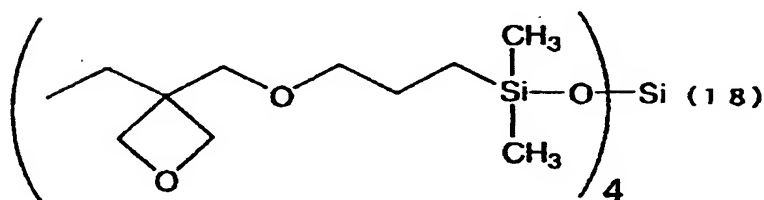
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wherein each L is individually an integer from 1-10.

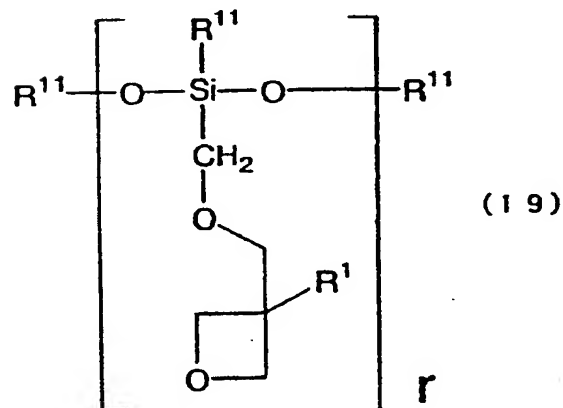




As specific examples of compounds having three or more oxetane rings in the molecule, compounds shown by the following formula (18) can be given.



10                   Compounds shown by the following formula  
(19) may comprise 1-10 oxetane rings:

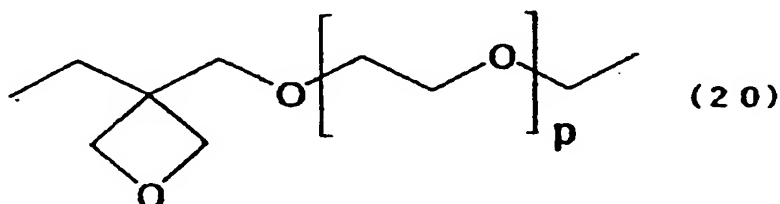


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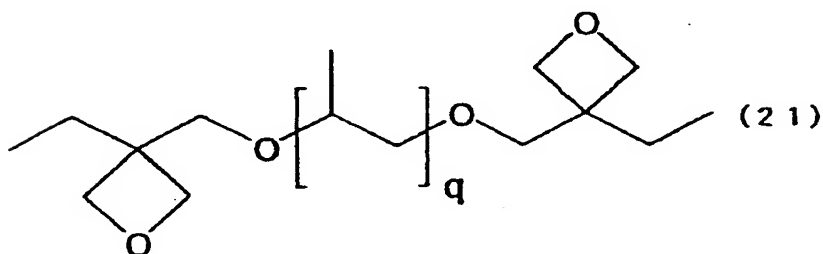
wherein R<sup>1</sup> is the same as defined for the formula (2),

$R^8$  is the same as defined for the formula (7),  $R^{11}$  represents an alkyl group having 1-4 carbon atoms or trialkylsilyl group (wherein each alkyl group individually is an alkyl group having 1-12 carbon atom), for example a trimethylsilyl group, triethylsilyl group, tripropylsilyl group, or tributylsilyl group, and  $r$  is an integer from 1-10.

Furthermore, other than the above-mentioned compounds, compounds having a polystyrene-reduced number average molecular weight measured by gel permeation chromatography of 1,000-5,000 can be given as examples of the oxetane compound (A). As examples of such compounds, compounds shown by the following formulas (20), (21), and (22) can be given:

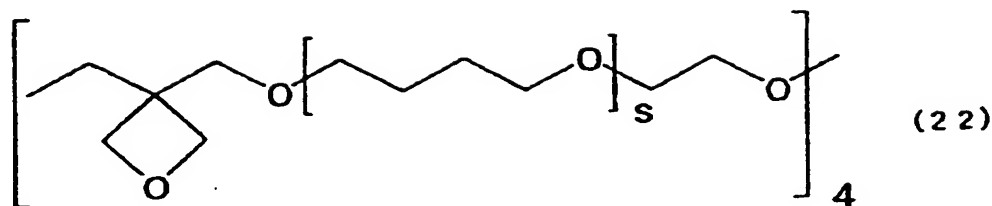


wherein  $p$  is an integer from 20-200:



20

wherein  $q$  is an integer from 15-100:



wherein s is an integer from 20-200.

Specific examples of the above-described  
 5 oxetane compound (A) are given below.

Compounds containing one oxetane ring in  
 the molecule:

3-ethyl-3-hydroxymethyloxetane, 3-(meth)allyloxymethyl-  
 3-ethyloxetane, (3-ethyl-3-  
 10 oxetanylmethoxy)methylbenzen, 4-fluoro-[1-(3-ethyl-3-  
 oxetanylmethoxy)methyl]benzene, 4-methoxy-[1-(3-ethyl-  
 3-oxetanylmethoxy)methyl]benzene, [1-(3-ethyl-3-  
 oxetanylmethoxy)ethyl] phenyl ether, isobutoxymethyl  
 (3-ethyl-3-oxetanylmethyl) ether, isobornyloxyethyl (3-  
 15 ethyl-3-oxetanylmethyl) ether, isobornyl (3-ethyl-3-  
 oxetanylmethyl) ether, 2-ethylhexyl (3-ethyl-3-oxetanyl  
 methyl) ether, ethyldiethylene glycol (3-ethyl-3-  
 oxetanylmethyl) ether, dicyclopentadiene (3-ethyl-3-  
 oxetanylmethyl) ether, dicyclopentenyl (3-  
 20 ethyl-3-oxetanyl methyl) ether, dicyclopentenyl (3-  
 ethyl-3-oxetanylmethyl) ether, tetrahydrofurfuryl (3-  
 ethyl-3-oxetanylmethyl) ether, tetrabromophenyl (3-  
 ethyl-3-oxetanylmethyl) ether, 2-tetrabromophenoxyethyl  
 (3-ethyl-3-oxetanylmethyl) ether, tribromophenyl (3-  
 25 ethyl-3-oxetanylmethyl) ether, 2-tribromophenoxyethyl  
 (3-ethyl-3-oxetanylmethyl) ether, 2-hydroxyethyl (3-  
 ethyl-3-oxetanyl methyl) ether, 2-hydroxypropyl (3-  
 ethyl-3-oxetanylmethyl) ether, butoxyethyl (3-ethyl-3-  
 oxetanylmethyl) ether, pentachlorophenyl (3-ethyl-3-

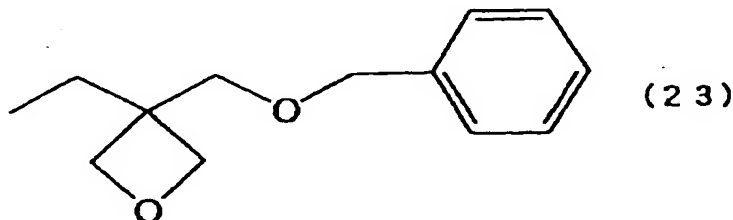


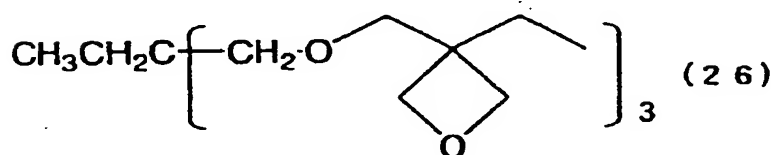
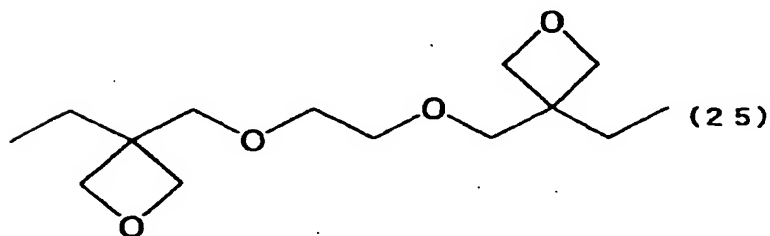
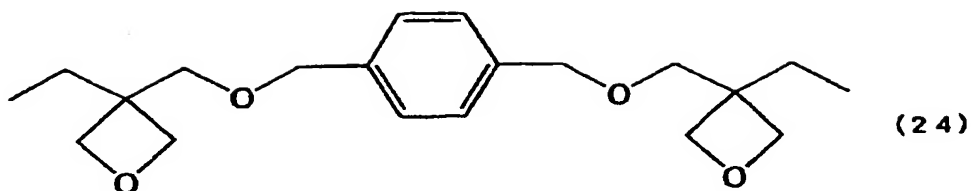
oxetanylmethyl) ether, pentabromophenyl (3-ethyl-3-oxetanylmethyl) ether, bornyl (3-ethyl-3-oxetanylmethyl) ether.

Compounds containing two or more oxetane  
5 rings in the molecule:  
3,7-bis(3-oxetanyl)-5-oxa-nonane, 3,3'-(1,3-(2-methylenyl)propanediylbis(oxymethylene))bis-(3-ethyloxetane), 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene, 1,2-bis[(3-ethyl-3-oxetanylmethoxy)methyl]ethane, 1,3-bis[(3-ethyl-3-oxetanylmethoxy)methyl]propane, ethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, dicyclopentenyl bis(3-ethyl-3-oxetanylmethyl) ether, triethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, tetraethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, 15 tricyclodecanediylldimethylene (3-ethyl-3-oxetanylmethyl) ether, trimethylolpropane tris(3-ethyl-3-oxetanylmethyl) ether, 1,4-bis(3-ethyl-3-oxetanylmethoxy)butane, 1,6-bis(3-ethyl-3-oxetanylmethoxy)hexane, pentaerythritol tris(3-ethyl-3-oxetanylmethyl) ether, pentaerythritol tetrakis(3-ethyl-3-oxetanylmethyl) ether, polyethylene glycol bis(3-ethyl-3-oxetanylmethyl) ether, dipentaerythritol hexakis(3-ethyl-3-oxetanylmethyl) ether, 25 dipentaerythritol pentakis(3-ethyl-3-oxetanylmethyl) ether, dipentaerythritol tetrakis(3-ethyl-3-oxetanylmethyl) ether, caprolactone-modified dipentaerythritol hexakis(3-ethyl-3-oxetanylmethyl) ether, caprolactone-modified dipentaerythritol 30 pentakis(3-ethyl-3-oxetanylmethyl) ether, ditrimethylolpropane tetrakis(3-ethyl-3-oxetanylmethyl) ether, EO-modified bisphenol A bis(3-ethyl-3-

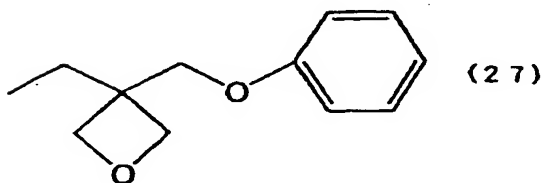
oxetanylmethyl) ether, PO-modified bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, EO-modified hydrogenated bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, PO-modified hydrogenated bisphenol A bis(3-ethyl-3-oxetanylmethyl) ether, EO-modified bisphenol F (3-ethyl-3-oxetanylmethyl) ether. These compounds can be used either individually or in combination of two or more.

Of these, oxetane compounds having 1-10, preferably 1-4, and particularly preferably two oxetane rings in the molecule are suitable as the component (A) of the resin composition of the present invention. Most preferred examples of compound (A) are, (3-ethyl-3-oxetanylmethoxy)methylbenzene shown by the following formula (23), 1,4-bis[(3-ethyl-3-oxetanylmethoxy)methyl]benzene shown by the following formula (24), 1,2-bis(3-ethyl-3-oxetanylmethoxy)ethane shown by the following formula (25), trimethylolpropane tris(3-ethyl-3-oxetanylmethyl) ether shown by the following formula (26), 3-ethyl-3-oxetanylmethoxybenzene shown by the following formula (27), and the compound shown by the above formula (19), which compounds can be used either individually in combinations of two or more.





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These oxetane compounds can be used either individually or in combinations of two or more.

The content of the component (A) in the resin composition of the present invention is preferably 10-80 wt%, and still more preferably 20-60 wt%. If the content is too low, the cationic polymerization rate (curing rate) of the resulting resin composition decreases, whereby the fabrication may require a long period of time, or the resolution may decrease. If the content is too high, toughness of the cured product may be reduced or the cationic

20

*5 oxetane cpd.*

polymerization rate (curing rate) tends to decrease.

Component (B): epoxy compound

The photocurable resin composition of the present invention comprises an epoxy compound. The epoxy compound used in the present invention has a three-membered epoxyethane structure and does not include a structure with four members or more such as an oxetane group. The epoxy compound used in the present invention contains a glycidyl group or epoxycyclohexyl group in the molecule. The number of epoxyethane structures included in the epoxy compound is one or more, preferably 2-15, and still more preferably 2-8 per molecule.

In the present invention, the combined use of the epoxy compound together with the oxetane compound (A) increases the photocuring rate, specifically, improves curability.

As the epoxy compound (B) used in the present invention, compounds containing an epoxycyclohexyl group and compounds containing a glycidyl group are preferable. The epoxycyclohexyl group-containing compounds exhibit superior cationic polymerizability. The glycidyl group-containing compounds provide a polymer with flexibility and increase the mobility of the polymerization system, thereby further improving curability.

Examples of the epoxycyclohexyl group-containing compounds include 3,4-epoxycyclohexylmethyl-  
3',4'-epoxycyclohexanecarboxylate, 2-(3,4-epoxycyclohexyl-5,5-spiro-3,4-epoxy)cyclohexane-meta-dioxane, bis(3,4-epoxycyclohexylmethyl)adipate,

bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, 3,4-epoxy-6-methylcyclohexyl-3',4'-epoxy-6'-methylcyclohexanecarboxylate, methylenebis(3,4-epoxycyclohexane), di(3,4-epoxycyclohexylmethyl) ether  
5 of ethylene glycol, ethylenebis(3,4-epoxycyclohexanecarboxylate,  $\epsilon$ -caprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, trimethylcaprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-  
10 epoxycyclohexanecarboxylate,  $\beta$ -methyl- $\delta$ -valerolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate.

Of these, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, bis(3,4-epoxycyclohexylmethyl)adipate,  $\epsilon$ -caprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, trimethylcaprolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate, and  $\beta$ -methyl- $\delta$ -  
20 valerolactone-modified 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate are preferable. 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate and bis(3,4-epoxycyclohexylmethyl)adipate are particularly preferable.

25 As commercially available products suitably used as these compounds, UVR-6100, UVR-6105, UVR-6110, UVR-6128, UVR-6200, UVR-6216 (manufactured by Union Carbide Corp.), Celoxide 2021, Celoxide 2021P, Celoxide 2081, Celoxide 2083, Celoxide 2085, Epolead GT-300,  
30 Epolead GT-301, Epolead GT-302, Epolead GT-400, Epolead 401, Epolead 403 (manufactured by Daicel Chemical

Industries, Ltd.), KRM-2100, KRM-2110, KRM-2199 (manufactured by Asahi Denka Kogyo Co., Ltd.), and the like can be given. These compounds can be used either individually or in combinations of two or more.

5                   Examples of the glycidyl group-containing epoxy compounds suitably used as the component (B) include bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol S diglycidyl ether, brominated bisphenol A diglycidyl ether, brominated  
10 bisphenol F diglycidyl ether, brominated bisphenol S diglycidyl ether, hydrogenated bisphenol A diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, hydrogenated bisphenol S diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl  
15 ether, glycerol triglycidyl ether, trimethylolpropane triglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether; polydiglycidyl ethers of polyether polyols obtained by the addition of one or more alkylene oxides to  
20 aliphatic polyhydric alcohols such as ethylene glycol, propylene glycol, and glycerol; diglycidyl esters of aliphatic long-chain dibasic acids; monodiglycidyl ethers of aliphatic higher alcohols; monodiglycidyl ethers of phenol, cresol, butyl phenol, or polyether  
25 alcohols obtained by the addition of alkylene oxide to these compounds; and glycidyl esters of higher fatty acids.

Of these, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, hydrogenated bisphenol A  
30 diglycidyl ether, hydrogenated bisphenol F diglycidyl ether, 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, glycerol triglycidyl ether,

trimethylolpropane triglycidyl ether, neopentyl glycol diglycidyl ether, polyethylene glycol diglycidyl ether, and polypropylene glycol diglycidyl ether are preferable.

5                   As commercially available products suitably used as the glycidyl group-containing compounds, UVR-6216 (manufactured by Union Carbide Corp.), Glycidole, AOEX24, Cyclomer A200 (manufactured by Daicel Chemical Industries, Ltd.), Epicoat 828, Epicoat 812, Epicoat  
10 1031, Epicoat 872, Epicoat CT508 (manufactured by Yuka-Shell K.K.), KRM-2400, KRM-2410, KRM-2408, KRM-2490, KRM-2720, KRM-2750 (manufactured by Asahi Denka Kogyo Co., Ltd.), and the like can be given. These compounds can be used either individually or in combinations of  
15 two or more as the component (B).

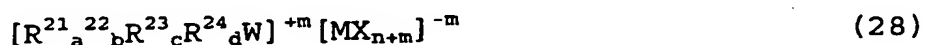
                  The content of the component (B) used in the photocurable resin composition of the present invention is usually 5-80 wt%, and preferably 20-70 wt%. If the content is too low, curability may be  
20 lowered. On the other hand, if the content is too high, viscosity of the resin composition increases, whereby the fabrication requires a long period of time.

#### (C) Photoacid generator

25                   The Photoacid generator (C) used in the photocurable resin composition of the present invention (hereinafter may be called "component (C)") generates a substance which initiates cationic polymerization of the component (A) upon exposure to energy rays such as  
30 light. The energy ray such as light used herein refers to visible light, ultraviolet light, infrared light, X-rays,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, and the like.

As examples of the compounds used as the component (C), an onium salt having a structure shown by the following formula (28) can be given. The onium salt liberates a Lewis acid upon exposure to light.

5



wherein the cation is an onium ion; W represents S, Se, Te, P, As, Sb, Bi, O, I, Br, Cl, or N≡N; R<sup>21</sup>, R<sup>22</sup>, R<sup>23</sup>, and R<sup>24</sup> represent individually the same or different organic group; a, b, c, and d independently represent an integer from 0 to 3, and provided that a+b+c+d is equal to the valence number of W. M represents a metal or metalloid which constitutes a center atom of a halide complex. Typical examples of M are B, P, As, Sb, Fe, Sn, Bi, Al, Ca, In, Ti, Zn, Sc, V, Cr, Mn, and Co. X represents a halogen atom such as a fluorine atom, chlorine atom, or bromine atom. m is a substantial electric charge of the halide complex ion and n is the valence of M.

Given as typical examples of the onium salts represented by the formula (28) are diphenyliodonium, 4-methoxydiphenyliodonium, bis(4-methylphenyl)iodonium, bis(4-tert-butylphenyl)iodonium, bis(dodecylphenyl)-iodonium, triphenylsulfonium, diphenyl-4-thiophenoxy-phenylsulfonium, bis[4-(diphenylsulfonio)-phenyl]-sulfide, bis[4-(di(4-(2-hydroxyethyl)phenyl)sulfonio)-phenyl]sulfide, and  $\eta^5$ -2,4-(cyclopentadienyl)-

[(1,2,3,4,5,6- $\eta$ )-(methylethyl)-benzene]-iron(1+).

30

Given as specific examples of the negative ion (MX<sub>n+m</sub>) in the above formula (28) are



tetrafluoroborate ( $\text{BF}_4^-$ ), hexafluorophosphate ( $\text{PF}_6^-$ ), hexafluoroantimonate ( $\text{SbF}_6^-$ ), hexafluoroarsenate ( $\text{AsF}_6^-$ ), and hexachloroantimonate ( $\text{SbCl}_6^-$ ).

Onium salts having an anion represented by  
5  $[\text{MX}_n(\text{OH})^-]$  can be used. Moreover, onium salts having other anions such as a perchloric acid ion ( $\text{ClO}_4^-$ ), trifluoromethanesulfonic acid ion ( $\text{CF}_3\text{SO}_3^-$ ), fluorosulfonic acid ion ( $\text{FSO}_3^-$ ), toluenesulfonic acid ion, trinitrobenzenesulfonic acid anion, and  
10 trinitrotoluenesulfonic acid anion can also be used.

Of these onium salts, aromatic onium salts are particularly effective as the photoacid generator of the component (C). For example, aromatic halonium salts disclosed in Japanese Patent Application Laid-  
15 open Nos. 151996/1975 and 158680/1975, VIA group aromatic onium salts disclosed in Japanese Patent Application Laid-open Nos. 151997/1975, 30899/1977, 55420/1981, and 125105/1980, VA group aromatic onium salts disclosed in Japanese Patent Application Laid-  
20 open No. 158698/1975, oxosulfoxonium salts disclosed in Japanese Patent Application Laid-open Nos. 8428/1981, 149402/1981, and 192429/1982, aromatic diazonium salts disclosed in Japanese Patent Application Laid-open No. 17040/1974, thiopyrylium salts disclosed in U.S. Patent  
25 No. 4,139,655, and the like are preferable. In addition, iron/allene complex initiators, aluminum complex/photolysis silicon compound initiators, and the like can also be given as examples.

As examples of commercially available  
30 products of the photoacid generator suitably used as the component (C), UVI-6950, UVI-6970, UVI-6974, UVI-6990 (manufactured by Union Carbide Corp.),

Adekaoptomer SP-150, SP-151, SP-170, SP-171, SP-172  
(manufactured by Asahi Denka Kogyo Co., Ltd.), Irgacure  
261 (manufactured by Ciba Specialty Chemicals Co.), CI-  
2481, CI-2624, CI-2639, CI-2064 (manufactured by Nippon  
5 Soda Co., Ltd.), CD-1010, CD-1011, CD-1012  
(manufactured by Sartomer Co., Ltd.), DTS-102, DTS-103,  
NAT-103, NDS-103, TPS-103, MDS-103, MPI-103, BBI-103  
(manufactured by Midori Chemical Co., Ltd.), PCI-061T,  
PCI-062T, PCI-020T, PCI-022T (manufactured by Nippon  
10 Kayaku Co., Ltd.), and the like can be given. Of these,  
UVI-6970, UVI-6974, Adekaoptomer SP-170, SP-171, SP-  
172, CD-1012, and MPI-103 are particularly preferable,  
because high photocuring sensitivity can be provided in  
the resulting resin composition.

15               These photoacid generators can be used  
either individually or in combinations of two or more  
as the component (C).

              The content of the component (C) used in  
the photocurable resin composition of the present  
20 invention is usually 0.1-10 wt%, preferably 0.2-6 wt%,  
and still more preferably 0.3-4 wt%. If the content of  
the component (C) is too low, photocurability of the  
resulting resin composition decreases, whereby a three-  
dimensional object exhibiting sufficient mechanical  
25 strength cannot be produced. On the other hand, if the  
content is too high, it becomes difficult to control  
cure depth of the resulting resin composition when used  
for photofabrication due to insufficient  
phototransmission, whereby the resulting three-  
30 dimensional objects may exhibit insufficient  
fabrication accuracy.

Elastomer particles (D) with an average particle diameter of 10-700 nm

The elastomer particles (D) with an average particle diameter of 10-700 nm used in the photocurable resin composition of the present invention (hereinafter may be called "component (D)") are elastomer particles comprising, for example, polybutadiene, polyisoprene, butadiene/acrylonitrile copolymer, styrene/butadiene copolymer, styrene/isoprene copolymer, ethylene/propylene copolymer, ethylene/ $\alpha$ -olefin copolymer, ethylene/ $\alpha$ -olefin/polyene copolymer, acrylic rubber, butadiene/(meth)acrylate copolymer, styrene/butadiene block copolymer, and styrene/isoprene block copolymer. Moreover, core-shell type particles produced by coating these elastomer particles with a methyl methacrylate polymer, methyl methacrylate/glycidyl methacrylate copolymer, and the like can also be used. These elastomer particles may optionally with the assistance of crosslinking acids can be crosslinked by a conventional method. Examples of crosslinking acids used in such a method, divinylbenzene, ethylene glycol di(meth)acrylate, diallylmaleate, triallylcyanurate, triallylisocyanurate, diallylphthalate, trimethylolpropane triacrylate and allyl methacrylate.

Examples of the core-shell type particles, are elastomer particles in which a core of partially crosslinked polybutadiene, polyisoprene, styrene/butadiene copolymer, styrene/isoprene copolymer, ethylene/propylene copolymer, ethylene/ $\alpha$ -

olefin copolymer, ethylene/ $\alpha$ -olefin/polyene copolymer, acrylic rubber, butadiene/(meth)acrylate copolymer, styrene/butadiene block copolymer, or styrene/isoprene block copolymer, is coated with for example a methyl  
5 methacrylate polymer, or methyl methacrylate/glycidyl methacrylate copolymer. The ratio of the core radius to the shell thickness of the core-shell type particles is usually from 1/2 to 1000/1, preferably from 1/1 to 200/1 (for example, if the core radius is 350 nm and  
10 the shell thickness is 10 nm, the ratio is expressed as 35/1).

Of these elastomer particles, elastomer particles in which a core of partially crosslinked polybutadiene, polyisoprene, styrene/butadiene  
15 copolymer, styrene/isoprene copolymer, butadiene/(meth)acrylate copolymer, styrene/butadiene block copolymer, and styrene/isoprene block copolymer is coated with a methyl methacrylate polymer or methyl methacrylate/glycidyl methacrylate copolymer are  
20 particularly preferable.

These elastomer particles can be prepared by a conventional method such as emulsion polymerization. The emulsion polymerization can be carried out by, for example, polymerizing the total  
25 amount of a monomer component in one reaction, polymerizing part of a monomer component first and then continuously or intermittently adding the remaining part of the monomer component to polymerize, polymerizing a monomer component while continuously  
30 adding the monomer component during polymerization, or polymerizing a monomer component using seed particles.

The average particle diameter of the

elastomer particles thus produced is 10-700 nm, and preferably 30-300 nm. If elastomer particles with an average particle diameter of less than 10 nm are used, not only may the resulting three-dimensional objects exhibit decreased impact resistance but also productivity and fabrication accuracy of the three-dimensional objects may be adversely affected due to the increased viscosity of the resin composition. On the other hand, if elastomer particles with an average particle diameter of more than 700 nm are used, the surface of the resulting three-dimensional object may become uneven or fabrication accuracy may decrease.

As examples of commercially available products of these core-shell type elastomer particles, Resinous Bond RKB (manufactured by Resinous Chemical Industries Co., Ltd.), Techno MBS-61, MBS-69 (manufactured by Techno Polymer Co., Ltd.), and the like can be given.

These elastomer particles can be used either individually or in combinations of two or more as the component (D).

The content of the component (D) used in the photocurable resin composition of the present invention is preferably 1-35 wt%, more preferably 3-30 wt%, and particularly preferably 5-20 wt%. If the content of the component (D) is too low, the resulting three-dimensional object may exhibit decreased impact resistance. On the other hand, if the content is too high, the resulting three-dimensional object may exhibit decreased fabrication accuracy.

Component (E): polyol

The polyol (E) used in the photocurable resin composition of the present invention as an optional component (hereinafter may be called "component (E)") is useful for providing photocurability in the resin composition as well as form stability (controlling deformation with time) and physical stability (controlling change in mechanical characteristics with time) for the photofabricated three-dimensional objects. The polyol used as the component (E) contains preferably two or more, and still more preferably from 2 to 6 hydroxyl groups in one molecule. If a polyol containing less than two hydroxyl groups in one molecule is used, photocurability of the resin composition may not be sufficiently improved, and mechanical characteristics, in particular, the modulus of elasticity of the resulting three-dimensional objects may decrease. If a polyol containing more than six hydroxyl groups in one molecule is used, the resulting three-dimensional objects may exhibit insufficient elongation and reduced moisture resistance.

As examples of such polyols, polyether polyols, polycaprolactone polyols, polyester polyols produced by modifying with polyester consisting of dibasic acid and diols, and the like can be given.

Of these, polyether polyols are preferable. For example, polyether polyols formed by modifying polyhydric alcohols containing three or more hydroxyl groups such as trimethylolpropane, glycerol, pentaerythritol, sorbitol, and sucrose, quadrol with a cyclic ether compound such as ethylene oxide

(hereinafter may be called "EO"), propylene oxide (hereinafter may be called "PO"), butylene oxide, and tetrahydrofuran can be given as examples. Specific examples include EO-modified trimethylolpropane, PO-  
5 modified trimethylolpropane, tetrahydrofuran-modified trimethylolpropane, EO-modified glycerol, PO-modified glycerol, tetrahydrofuran-modified glycerol, EO-modified pentaerythritol, PO-modified pentaerythritol, tetrahydrofuran-modified pentaerythritol, EO-modified  
10 sorbitol, PO-modified sorbitol, EO-modified sucrose, PO-modified sucrose, EO-modified quadrol, polyoxyethylenediol, polyoxypropylenediol, polyoxytetramethylenediol, polyoxybutylenediol, polyoxybutylene-oxyethylene copolymer diol, and the  
15 like. Of these, EO-modified trimethylolpropane, PO-modified trimethylolpropane, PO-modified glycerol, and PO-modified sorbitol are preferable.

As examples of commercially available products of the polyether polyols used as the component  
20 (E), Sunnix TP-400, GP-600, GP-1000, SP-750, GP-250, GP-400, GP-600 (manufactured by Sanyo Chemical Industries, Ltd.), TMP-3 Glycol, PNT-4 Glycol, EDA-P-4, EDA-P-8 (manufactured by Nippon Nyukazai Co., Ltd.), G-300, G-400, G-700, T-400, EDP-450, SP-600, SC-800  
25 (manufactured by Asahi Denka Kogyo Co., Ltd.), and the like can be given.

As specific examples of the polycaprolactone polyols, caprolactone-modified trimethylolpropane, caprolactone-modified glycerol,  
30 caprolactone-modified pentaerythritol, caprolactone-modified sorbitol, and the like can be given.

Examples of commercially available products

- 30 -

of the polycaprolactone polyol include TONE 0301, TONE 0305, TONE 0310 (manufactured by Union Carbide Corp.), and the like. Examples of commercially available products of the polyester polyol include PLACCEL 303, 5 PLACCEL 305, PLACCEL 308 (manufactured by Daicel Chemical Industries, Ltd.), and the like.

These polyols can be used either individually or in combinations of two or more as the component (E).

10 The molecular weight of the polyol used as the component (E) is preferably 100-50,000, and still more preferably 160-20,000. If the molecular weight of the polyol used as the component (E) is too small, the three-dimensional object exhibiting form stability and 15 physical stability cannot be formed depending on the resulting resin composition. If the molecular weight of the polyol is too great, viscosity of the resin composition may increase, thereby reducing the modulus of elasticity of the photofabricated three-dimensional 20 objects.

The content of the component (E) used in the photocurable resin composition of the present invention is usually 0-35 wt%, and preferably 0-25 wt%. If the content of the component (E) is too great, 25 photocurability of the resin composition may decrease, thereby reducing the modulus of elasticity of the resulting three-dimensional objects.

#### Ethylenically unsaturated monomer (F)

30 The ethylenically unsaturated monomer (F) optionally used in the photocurable resin composition of the present invention (hereinafter may be called

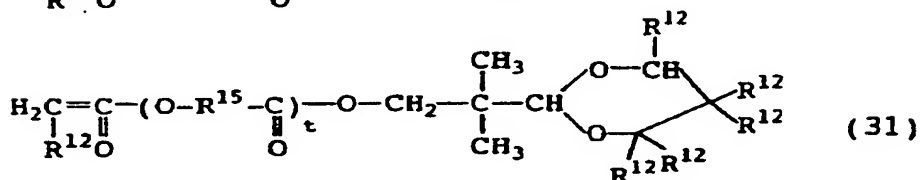
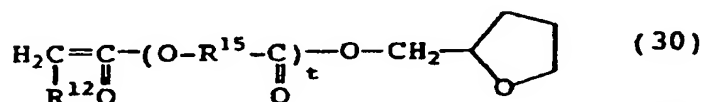
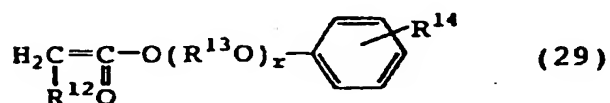


"component (F)" contains an ethylenically unsaturated bond (C=C) in the molecule. As examples of the component (F), monofunctional monomers containing one ethylenically unsaturated bond in one molecule and  
5 polyfunctional monomers containing two or more, and preferably three or more ethylenically unsaturated bonds in one molecule can be given.

Examples of the monofunctional monomers suitably used as the component (F) include acrylamide,  
10 (meth)acryloylmorpholine, 7-amino-3,7-dimethyloctyl (meth)acrylate, isobutoxymethyl (meth)acrylamide, isobornyloxyethyl (meth)acrylate, isobornyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, ethyldiethylene glycol (meth)acrylate, t-octyl  
15 (meth)acrylamide, diacetone (meth)acrylamide, dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, lauryl (meth)acrylate, dicyclopentadiene (meth)acrylate, dicyclopentenylloxyethyl (meth)acrylate, dicyclopentenyl  
20 (meth)acrylate, N,N-dimethyl (meth)acrylamidetetrachlorophenyl (meth)acrylate, 2-tetrachlorophenoxyethyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, tetrabromophenyl (meth)acrylate, 2-tetrabromophenoxyethyl (meth)acrylate, 2-trichlorophenoxyethyl (meth)acrylate, tribromophenyl (meth)acrylate, 2-tribromophenoxyethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, vinylcaprolactam, N-vinylpyrrolidone,  
25 phenoxyethyl (meth)acrylate, butoxyethyl (meth)acrylate, pentachlorophenyl (meth)acrylate, pentabromophenyl (meth)acrylate, polyethylene glycol

mono(meth)acrylate, polypropylene glycol mono(meth)acrylate, bornyl (meth)acrylate, methyltriethylene diglycol (meth)acrylate, and compounds shown by the following formulas (29) - (31).

5



wherein  $R_{12} = H, Me$

10  $R_{13}$  and  $R_{15}$  are alkylene groups having 1-20 C-atoms

$R_{14}$  = H or alkylene group having 1-20 C-atoms

$r$ ,  $t$  are integers from 0 to 100

Of these monofunctional monomers, isobornyl  
15 (meth)acrylate, lauryl (meth)acrylate, and phenoxyethyl  
(meth)acrylate are particularly preferable.

As examples of commercially available products of these monofunctional monomers, ARONIX M-101, M-102, M-111, M-113, M-117, M-152, TO-1210 (manufactured by Toagosei Co., Ltd.), KAYARAD TC-110S, R-564, R-128H (manufactured by Nippon Kayaku Co., Ltd.), Viscoat 192, 220, 2311HP, 2000, 2100, 2150, 8F, 17F (manufactured by Osaka Organic Chemical Industry Co., Ltd.), and the like can be given.

Examples of the polyfunctional monomers suitably used as the component (F) include ethylene glycol di(meth)acrylate, dicyclopentenyl di(meth)acrylate, triethylene glycol diacrylate, 5 tetraethylene glycol di(meth)acrylate, tricyclodecanediylldimethylene di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, caprolactone-modified tris(2-hydroxyethyl)isocyanurate 10 tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, ethylene oxide (hereinafter may be abbreviated as "EO") modified trimethylolpropane tri(meth)acrylate, propylene oxide (hereinafter may be abbreviated as "PO") modified trimethylolpropane 15 tri(meth)acrylate, tripropylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, both-terminal (meth)acrylic acid adduct of bisphenol A diglycidyl ether, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, pentaerythritol 20 tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, polyester di(meth)acrylate, polyethylene glycol di(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, dipentaerythritol tetra(meth)acrylate, caprolactone- 25 modified dipentaerythritol hexa(meth)acrylate, caprolactone-modified dipentaerythritol penta(meth)acrylate, ditrimethylolpropane tetra(meth)acrylate, EO-modified bisphenol A di(meth)acrylate, PO-modified bisphenol A 30 di(meth)acrylate, EO-modified hydrogenated bisphenol A di(meth)acrylate, PO-modified hydrogenated bisphenol A di(meth)acrylate, EO-modified bisphenol F

di(meth)acrylate, (meth)acrylate of phenol novolak polyglycidyl ether, and the like.

As examples of commercially available products of these polyfunctional monomers, SA 1002  
5 (manufactured by Mitsubishi Chemical Corp.), Viscoat 195, 230, 260, 215, 310, 214HP, 295, 300, 360, GPT, 400, 700, 540, 3000, 3700 (manufactured by Osaka Organic Chemical Industry Co., Ltd.), KAYARAD R-526, HDDA, NPGDA, TPGDA, MANDA, R-551, R-712, R-604, R-684,  
10 PET-30, GPO-303, TMPTA, THE-330, DPHA, DPHA-2H, DPHA-2C, DPHA-2I, D-310, D-330, DPCA-20, DPCA-30, DPCA-60, DPCA-120, DN-0075, DN-2475, T-1420, T-2020, T-2040, TPA-320, TPA-330, RP-1040, RP-2040, R-011, R-300, R-205 (manufactured by Nippon Kayaku Co., Ltd.), ARONIX M-  
15 210, M-220, M-233, M-240, M-215, M-305, M-309, M-310, M-315, M-325, M-400, M-6200, M-6400 (manufactured by Toagosei Co., Ltd.), Lite Acrylate BP-4EA, BP-4PA, BP-2EA, BP-2PA, DCP-A (manufactured by Kyoeisha Chemical Co., Ltd.), New Frontier BPE-4, TEICA, BR-42M, GX-8345  
20 (manufactured by Daiichi Kogyo Seiyaku Co., Ltd.), ASF-400 (manufactured by Nippon Steel Chemical Co., Ltd.), Lipoxy SP-1506, SP-1 507, SP-1 509, VR-77, SP-4010, SP-4060 (manufactured by Showa Highpolymer Co., Ltd.), NK Ester A-BPE-4 (manufactured by Shin-Nakamura Chemical  
25 Co., Ltd.), and the like can be given.

Each of the above monofunctional and polyfunctional monomers can be used either individually or in combinations of two or more, or in combinations of at least one monofunctional monomer and at least one  
30 polyfunctional monomer as the component (F). It is preferable that 60 wt% or more of the component (F) consists of the polyfunctional monomers having three or

more ethylenically unsaturated bonds in one molecule. The percentage of the polyfunctional monomers of component (F) having three or more ethylenically unsaturated bonds is more preferably 70 wt% or more, even more preferably 80 wt% or more, and particularly preferably 100 wt%. If the content of these polyfunctional monomers is less than 60 wt%, photocurability of the resin composition may decrease and the resulting three-dimensional objects tends to exhibit deformation with time.

These polyfunctional monomers having three or more ethylenically unsaturated bonds can be selected from the group consisting of the above-mentioned tri(meth)acrylate compounds, tetra(meth)acrylate compounds, penta(meth)acrylate compounds, and hexa(meth)acrylate compounds. Of these, trimethylolpropane tri(meth)acrylate, EO-modified trimethylolpropane tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, and ditrimethylolpropane tetra(meth)acrylate are particularly preferable.

The content of the component (F) used in the photocurable resin composition of the present invention is usually 0-45 wt%, preferably 3-35 wt%, and particularly preferably 5-10 wt%. If the content of the component (F) is too low, the resulting resin composition may exhibit decreased photocurability, whereby the three-dimensional object exhibiting sufficient mechanical strength cannot be formed. If the content is too high, the resulting resin composition may exhibit shrinkage during photocuring and the resulting three-dimensional objects may exhibit

insufficient heat resistance and decreased moisture resistance.

Radical photopolymerization initiator (G)

5                   The radical photopolymerization initiator (G) of the photocurable resin composition of the present invention (hereinafter also called "component (G)") decomposes by exposure to energy rays such as light to initiate the radical polymerization of the  
10 component (G) with radicals. The energy ray such as light used herein refers to visible light, ultraviolet light, infrared light, X-rays,  $\alpha$ -rays,  $\beta$ -rays,  $\gamma$ -rays, and the like.

                  Specific examples of the radical  
15 photopolymerization initiators used as the component (G) include acetophenone, acetophenone benzyl ketal, anthraquinone, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one, carbazole, xanthone, 4-chlorobenzophenone, 4,4'-diaminobenzophenone, 1,1-dimethoxydeoxybenzoin, 3,3'-dimethyl-4-  
20 methoxybenzophenone, thioxanethone compounds, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholino-propan-2-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, triphenylamine, 2,4,6-  
25 trimethylbenzoyldiphenylphosphine oxide, bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide, benzyl methyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2-hydroxy-2-methyl-1-phenylpropan-1-one, fluorenone, fluorene, benzaldehyde, benzoin ethyl ether, benzoin  
30 propyl ether, benzophenone, Michler's ketone, 3-methylacetophenone, 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone (BTTB), combinations

of BTTB and dye sensitizers such as xanthene, thioxanthene, cumarin, and ketocumarin, and the like. Of these, benzyl dimethyl ketal, 1-hydroxycyclohexyl phenyl ketone, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, and the like are particularly preferable.

These radical photopolymerization initiators can be used either individually or in combinations of two or more as the component (G).

10 The content of the component (G) used in the photocurable resin composition of the present invention is usually 0-10 wt%, and preferably 0.1-8 wt%. If the content is too low, the radical polymerization rate (curing rate) of the resulting resin composition may decrease, whereby the fabrication may require a long period of time or the resolution may be reduced. If the content is too high, an excess amount of the polymerization initiator may decrease the curing characteristics of the resin composition or  
15 adversely affect the moisture resistance or heat resistance of the resulting three-dimensional objects.  
20

#### Other components

Photosensitizers (polymerization accelerator), reactive diluents, and the like can be added to the photocurable resin composition of the present invention as optional components other than the components (A)-(G), insofar as the effects of the resin composition are not impaired.

30 As examples of the photosensitizers, amine compounds such as triethanolamine, methyldiethanolamine, triethylamine, and diethylamine,

thioxanethone, derivatives of thioxanethone,  
anthraquinone, derivatives of anthraquinone,  
anthracene, derivatives of anthracene, perylene,  
derivatives of perylene, benzophenone, benzoin  
5 isopropyl ether, and the like can be given. As the  
reactive diluents, cationically polymerizable  
substances which are copolymerizable with the  
components (A) and (B) and can decrease the viscosity  
of composition solution are preferable.

10                   Moreover, various additives may be added to  
the photocurable resin composition of the present  
invention as other optional components insofar as the  
objects and effects of the present invention are not  
impaired. Examples of such additives include polymers  
15 or oligomers such as an epoxy resin, polyamide,  
polyamideimide, polyurethane, polybutadiene,  
polychloroprene, polyether, polyester, styrene-  
butadiene block copolymer, petroleum resin, xylene  
resin, ketone resin, cellulose resin, fluorine-  
20 containing oligomer, silicone-containing oligomer, and  
polysulfide oligomer, polymerization inhibitors such as  
phenothiazine and 2,6-di-t-butyl-4-methylphenol,  
polymerization initiation adjuvant, leveling agents,  
wettability improvers, surfactants, plasticizers, UV  
25 absorbers, silane coupling agents, inorganic fillers,  
pigments, dyes, and the like.

The photocurable resin composition of the  
present invention can be produced by mixing the above  
components (A)-(G) homogeneously together with the  
30 optional components as required.

Viscosity of the photocurable resin  
composition at 25°C is preferably 50-2,000 cps



(mPa.sec), and still more preferably 70-1,500 cps (mPa.sec).

The photocurable liquid resin composition of the present invention thus produced is suitably used as a photocurable liquid resin material for the photofabrication of three-dimensional objects. In the photofabrication, the photocurable resin composition of the present invention is provided with energy required for curing by being selectively irradiated with light such as visible light, ultraviolet light, or infrared light to form a three-dimensional object with a desired shape.

As the means of selectively irradiating the photocurable resin composition, various means can be employed without specific limitations. For example, a means of irradiating the composition while scanning with laser beams or focused rays converged by lenses, mirrors, and the like, a means of irradiating the composition with unfocused rays via a mask having a phototransmission area with a specified pattern, a means of irradiating the composition via optical fibers corresponding to a specified pattern of a photoconductive material comprising bundled multiple optical fibers, and the like can be employed. A mask which electrooptically forms a mask image consisting of a phototransmission area and a non-phototransmission area in accordance with a specified pattern by the same principle as that of a liquid crystal display can be used. If minute parts or high dimensional accuracy are required in the objective three-dimensional object, a means of scanning with laser beams with a small spot diameter is preferably employed.

The surface of the resin composition in a vessel to be irradiated (for example, scanning plane of focused rays) may be the liquid surface of the resin composition or the interface between the resin composition and the wall of the vessel. In the latter case, the composition can be irradiated either directly or indirectly via the wall of the vessel.

In the photofabrication of three-dimensional objects, after curing a predetermined area of the resin composition, the cured area is laminated by continuously or gradually moving the irradiation spot (irradiation surface) from the cured area to the uncured area to form an objective three-dimensional object. The irradiation spot can be moved by, for example, moving any one of a light source, vessel of the resin composition, or the cured area of the resin composition, or providing additional resin composition to the vessel.

A typical example of the photofabrication is as follows. The resin composition is provided on a support stage capable of moving up and down placed inside the container and is minutely lowered (submerged) to form a thin layer (1) of the resin composition. This thin layer (1) is selectively irradiated to form a solid cured resin layer (1). The liquid resin composition is provided on this cured resin layer (1) to form a thin layer (2). This thin layer (2) is selectively irradiated to form a cured resin layer (2) integrally laminated on the cured resin layer (1). This step is repeated for a certain number of times while using either the same or different irradiation patterns to form a three-dimensional object

consisting of integrally laminated cured resin layers (n).

The resulting three-dimensional object is then removed from the vessel. After the residual  
5 unreacted resin composition remaining on the surface is removed, the three-dimensional object is optionally washed. As washing agents, alcohol-type organic solvents such as isopropyl alcohol and ethyl alcohol, ketone-type organic solvents such as acetone, ethyl  
10 acetate, and methyl ethyl ketone, aliphatic organic solvents represented by terpenes, and low-viscosity heat curable or photocurable resins can be given.

When fabricating a three-dimensional object having surface smoothness, it is preferable to wash the  
15 surface of the three-dimensional object using a heat curable or photocurable resin. In this case, postcure by irradiating with heat or light is required in accordance with the type of curable resin used for washing. Since not only the resins on the surface of  
20 the object but also the uncured resin composition remaining inside the three-dimensional objects can be cured by the postcure, it is also preferable to perform the postcure after washing with organic solvents.

Furthermore, it is preferable to coat the  
25 surface of the three-dimensional object with heat curable or photocurable hard coatings in order to improve the surface hardness and heat resistance of the three-dimensional objects after washing the object. As such hard coating materials, organic coatings such as  
30 an acrylic resin, epoxy resin, and silicone resin or inorganic hard coatings can be used. These hard coatings can be used either individually or in

combinations of two or more.

The three-dimensional object formed by photocuring the photocurable resin composition for photofabrication of three-dimensional objects of the present invention exhibits superior fabrication accuracy, a large modulus of elasticity, and excellent folding endurance with little change over time. Therefore, the three-dimensional object can be suitably used as mechanical parts, machine housings, and prototypes for such products.

#### Examples

The present invention will be described in detail by examples, which should not be construed as limiting the present invention.

#### Example 1

A stirrer was charged with 50 parts by weight of 1,4-bis(3-ethyl-3-oxetanylmethoxy)methylbenzene (Component (A)), 2 parts by weight of triallylsulfonium hexafluoroantimonate (UVI-6974: manufactured by Union Carbide Corp.) (Component (C)), 8 parts by weight of elastomer particles with an average particle diameter of 200 nm produced by emulsion polymerization (core: partially crosslinked styrene/butadiene copolymer, shell: methyl methacrylate/glycidyl methacrylate) (Component (D)), 30 parts by weight of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (UVR-6110: manufactured by Union Carbide Corp.) (component B1), 10 parts by weight 1,6-hexanediol diglycidyl ether (Epolite 1600: manufactured by Kyoeisha Chemical Co., Ltd.) (Component

(B)). The mixture was stirred at 60°C for 3 hours to prepare the photocurable liquid resin composition of the present invention.

Example 2-8 and Comparative Example 1-4

- 5                      Photocurable resin compositions were prepared in the same manner as in Example 1 except the components (A)-(G) were stirred and mixed according to the formulations shown in Table 1. The values for each component in Table 1 are given in "part(s) by weight".
- 10 The viscosity of all the resin compositions of the Examples and Comparative Examples were suitable for the photofabrication of three-dimensional objects.

Σ 50 pbw

Component	Example										Comparative example			
	1	2	3	4	5	6	7	8	9	10	1	2	3	4
A Oxetane compound *1	50	40	30	50	30	30	40	30	90	50	-	-	-	15
B Oxetane compound *2	-	-	-	-	-	10	-	-	-	-	-	-	-	-
C Epoxycyclohexane *6	30	30	30	30	30	30	30	30	8	38	60	14	-	-
D Epoxycyclohexane *7	-	10	15	10	15	10	5	-	-	-	15	-	-	-
E 1,6-hexanediol	10	10	15	-	-	-	10	-	-	10	15	-	-	-
F diglycidyl ether	-	-	-	-	15	10	-	15	-	-	-	-	-	-
G Neopentyl glycol glycidyl ether	-	-	-	-	-	-	-	-	-	-	-	-	-	-
H Photoacid generator *3	2	2	2	2	2	2	2	2	2	2	2	2	2	2
I Elastomer particles 200 nm *4	8	8	8	8	-	8	6	8	-	-	8	8	-	8
J Elastomer particles 50 nm -5	-	-	-	-	8	-	-	-	-	-	-	-	-	-
K Propylene oxide-modified glycerol *8	-	-	-	-	-	-	5	-	-	-	-	-	-	-
L Trimethylolpropane triacrylate	-	-	-	-	-	-	-	14	-	-	-	-	-	60
M 1-hydroxy phenyl ketone	-	-	-	-	-	-	-	1	-	-	-	-	-	1
Property														
Curability	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Bad	Excel-lent	Bad	Excel-lent
Modulus of elasticity (after 1 day)	160	150	155	170	157	150	153	150	110	172	182	195	-	-
Modulus of elasticity (after 30 days)	155	146	150	165	152	146	148	154	120	165	170	210	-	-
Folding endurance	O	O	O	O	O	O	O	O	O	X	X	X	X	X
Warping amount of fabricated object	Good	Excel-lent	Excel-lent	Good	Excel-lent	Excel-lent	Excel-lent	Excel-lent	Was not formed	Good	Was not formed	Bad	Was not formed	Bad
Fabrication accuracy	O	O	O	O	O	O	O	O	Was not formed	O	Was not formed	X	Was not formed	X

Details of \*1 to \*8 in Table 1 are as follows.

\*1: 1,4-bis(3-ethyl-3-oxetanylmethoxy)methylbenzene

\*2: 3-ethyl[3-(phenoxy)methyl]oxetane

\*3: Triallylsulfonium hexafluoroantimonate (UVI-6974:  
5 manufactured by Union Carbide Corp.)

\*4: Elastomer particles with an average particle  
diameter of 200 nm produced by emulsion  
polymerization (core: partially crosslinked  
styrene/butadiene copolymer, shell: methyl  
10 methacrylate/glycidyl methacrylate)

\*5: Elastomer particles with an average particle  
diameter of 50 nm produced by emulsion  
polymerization (core: partially crosslinked  
styrene/butadiene copolymer, shell: methyl  
15 methacrylate/glycidyl methacrylate)

\*6: 3,4-epoxycyclohexylmethyl-3',4'-  
epoxycyclohexanecarboxylate (UVR-6110: manufactured  
by Union Carbide Corp.)

\*7: Bis(3,4-epoxycyclohexylmethyl)adipate

20 \*8: Propylene oxide-modified glycerol (Sunnix GP-400:  
manufactured by Sanyo Chemical Industries, Ltd.)

Each photocurable resin composition  
prepared in Examples 1-8 and Comparative Examples 1-4  
25 was evaluated according to the following method.

#### Curability

The photocurable resin composition was  
selectively irradiated using a photofabrication  
30 apparatus "Solid Creator JSC-2000" (manufactured by  
SONY Corp.) equipped with an Ar ion laser as a light  
source (wavelength: 351nm, 365nm) with a laser spot

diameter of 200  $\mu\text{m}$  and a laser power of 100 mW at the irradiation surface (liquid surface) while changing the scanning speed from 100 to 1,000 mm/second to measure a minimum energy value at which the resin composition is cured. The evaluation criteria were as follows. When the minimum energy value was less than 20  $\text{mJ}/\text{cm}^2$ , curability was determined as "excellent"; when 20 to less than 30  $\text{mJ}/\text{cm}^2$ , curability was determined as "good"; and when 30  $\text{mJ}/\text{cm}^2$  or more or when cured products were not produced, curability was determined as "bad".

#### MODULUS OF ELASTICITY

15

##### (1) Preparation of test specimen:

The composition was applied to a glass plate using an applicator to form a film with a thickness of 200  $\mu\text{m}$ . The surface of the film was irradiated with UV light at a dose of 0.5  $\text{J}/\text{cm}^2$  using a conveyer curing apparatus equipped with a metal halide lamp to prepare a semi-cured resin film. The semi-cured resin film was peeled off the glass plate and put on a releasable paper. The side of the semi-cured resin film opposite to the previously irradiated side was then irradiated with UV light at a dose of 0.5  $\text{J}/\text{cm}^2$  to form a cured resin film.

The cured resin film thus prepared was allowed to stand under the following conditions to prepare test specimens ① and ②.

Test specimen ①: Allowed to stand in a thermo-hygrostat



at a temperature of 23°C and a relative humidity of 50% for 24 hours.

Test specimen ②: Allowed to stand in a thermo-hygrostat at a temperature of 23°C and a relative humidity of 50% for 30 days.

(2) Measurement:

Modulus of elasticity of each of the test specimen ① (for measurement of initial value) and test specimen ② (for measurement of change with time) was measured at a tensile rate of 1 mm/min and a bench mark distance of 25 mm in a thermo-hygrostat at a temperature of 23°C and a relative humidity of 50%.

15 Folding endurance

A cured resin film prepared under the same conditions as the test specimen ① for the measurement of modulus of elasticity was used as a test specimen. The folding endurance test was carried out by repeatedly folding the test specimen at a frequency of 60 times/sec. while applying a load of 1 kgf using an MIT folding endurance tester to measure the number of folds until the test specimen broke. A test specimen which broke at the folded part after 30 or more folds was rated as "O", a test specimen which broke after 40 or more folds was rated as "⊙", a test specimen which broke after less than 25 folds was rated as "X", and a test specimen which broke after 26-29 folds was rated as "Δ".

## AMOUNT OF WARPING OF THREE-DIMENSIONAL OBJECT

### (1) Preparation of test specimen:

The photocurable resin composition was  
5 selectively irradiated with a laser beam with a laser  
power of 100 mW at the irradiation surface (liquid  
surface) and a scanning speed at which the cure depth  
of each composition is 0.3 mm using the above  
photofabrication apparatus (JSC-2000) to form a cured  
10 resin layer (thickness: 0.20 mm). This step was  
repeated to form a measurement model (hereinafter  
called "warping model") shown in Fig. 1 (1). The  
warping model was then removed from the  
photofabrication apparatus. The resin composition  
15 adhering to the surface of the warping model was wiped  
off and an excess resin composition was removed from  
the model by washing with a terpene solvent.

### (2) Measurement:

20 A leg 11 of a warping model 10 was secured  
to a horizontal stand 20 as shown in Fig. 1 (2). The  
distance between the horizontal stand 20 and the bottom  
end of the leg 12 (uplifting amount) was evaluated as  
the warping amount (initial value). The compositions  
25 were rated as "excellent", "good", or "bad" in the  
order of the warping amount.

### Fabrication accuracy

Fabrication accuracy of the three-  
30 dimensional objects was evaluated by taking the  
dimensions of the three-dimensional objects formed from  
each liquid resin.

(1) Formation of three-dimensional object:

A test specimen shaped like an "H" was formed under the same conditions as in the above "Amount of warping of three-dimensional object". The three-dimensional objects were conditioned by being allowed to stand in a thermo-hygrostat at a temperature of 23°C and a relative humidity of 50% for 24 hours.

(2) Measurement of dimensional accuracy of three-dimensional object:

Dimensions A, B, and C shown in Fig. 2 of the three-dimensional objects were taken using a caliper graduated in 0.01 mm. The dimensional differences between A and B and between C and B were determined according to the following formulas (I) and (II).

Dimensional difference between A and B = (A-B) (I)

Dimensional difference between C and B = (C-B) (II)

Dimensional accuracy of the three-dimensional object was evaluated as follows.

- Both the absolute values of dimensional differences between A and B and between C and B were less than 0.1 mm: "⊙"
- One of the absolute values of dimensional differences between A and B and between C and B was less than 0.1 mm and the other was 0.1 or more but less than 0.2 mm: "○"
- Both the absolute values of dimensional differences between A and B and between C and B were 0.1 mm or more but less than 0.2 mm: "Δ"

- One of the absolute values of dimensional differences between A and B and between C and B was 0.2 mm or more, or no three-dimensional object was formed: "X"

As is clear from Table 1, cured products of the compositions according to Examples 1-8 excelled in curability and fabrication accuracy and exhibited a large modulus of elasticity, a small amount of warping, and, in particular, excellent folding endurance.

On the contrary, the composition of Comparative Example 1 in which the epoxy compound (B) was not used exhibited poor curability. Although the composition was not cured under the same curing conditions as the Examples, the composition was cured by taking time to measure the modulus of elasticity and folding endurance. As for the warping amount and fabrication accuracy of the three-dimensional object, the composition was referred to as "was not formed" because the composition was not cured under the same conditions as in the Example. A cured product of the composition of Comparative Example 2 in which the elastomer particles (D) were not used exhibited inferior folding endurance. The composition of Comparative Example 3 in which the oxetane compound (A) was not used exhibited poor curability. Although the composition was not cured under the same curing conditions as the Examples, the composition was cured by taking time to measure the modulus of elasticity and folding endurance. As for the warping amount and fabrication accuracy of the three-dimensional object, the composition was referred to as "was not formed" because the composition was not cured under the same conditions as in the Example. The composition of

Comparative Example 4 in which an excess amount of the ethylenically unsaturated monomer (F) was used exhibited superior curability but the three-dimensional object exhibited a large amount of warping and inferior  
5 fabrication accuracy.

The photocurable resin composition of the present invention comprises elastomer particles and exhibits excellent photocurability. The cured product of the composition exhibited a high modulus of  
10 elasticity, of which the decrease after 30 days was at an acceptable level, and superior fabrication accuracy, and the three-dimensional object of the cured product exhibited a small amount of warping. In particular, the cured product of the photocurable resin composition of  
15 the present invention exhibited remarkably superior folding endurance in comparison with conventional photocurable resins. Therefore, the photocurable resin composition can be suitably used for manufacturing three-dimensional objects such as prototypes for  
20 machine parts.

Fig. 1 is a diagram illustrating a model and a method for measuring a warping amount of cured products formed from photocurable compositions of the Examples and Comparative Examples.

25 Fig. 2 is a schematic view of a model for measuring fabrication accuracy (dimensional accuracy) of cured products formed from photocurable compositions of the Examples and Comparative Examples.

CLAIMS

1. Photocurable resin composition for  
5 photofabrication of three-dimensional objects  
comprising  
(A) 5-80 parts by weight of an oxetane compound,  
(B) 5-80 parts by weight of an epoxy compound,  
(C) 0,1-10 parts by weight of a photoacid  
10 generator,  
(D) 1-35 parts by weight of elastomer particles  
with an average particle diameter of 10-700 nm,  
(E) 0-35 parts by weight of a polyol compound,  
(F) 0-45 parts by weight of an ethylenically  
15 unsaturated monomer, and  
(G) 0-10 parts by weight of a radical  
photopolymerization initiator.
2. Photocurable resin composition according to claim  
1, wherein the oxetane compound (A) contains two  
20 oxetane rings.
3. Photocurable resin composition according to  
claims 1 or 2, wherein the epoxy compound (B)  
contains an epoxycyclohexylgroup or  
glycidylgroup.
- 25 4. Photocurable resin composition according to any  
of claims 1-3, wherein the photoacid generator is  
an aromatic onium salt.
5. Photocurable resin composition according to any  
of claims 1-4 wherein the particles (D) comprise  
30 elastomer particles in which a core of partially  
crosslinked polybutadiene, polyisoprene,  
styrene/butadiene copolymer, styrene/isoprene

- copolymer, butadiene/(meth)acrylate copolymer, styrene/butadiene block copolymer, and styrene/isoprene block copolymer is coated with a methyl methacrylate polymer or methyl methacrylate/glycidyl methacrylate copolymer.
- 5
6. Photocurable resin composition according to any of claims 1-5, wherein polyol (E) contains from 2 to 6 hydroxyl groups.
7. Use of the photocurable resin composition as
- 10 defined in claims 1-6 in the photofabrication of three dimensional objects.
8. A three dimensional object obtainable by photofabrication of the photocurable resin composition as defined in claims 1-6.
- 15 9. Use of the three dimensional object as defined in claim 8 for design models and prototypes for mechanical parts.

1/2

## Explanation of Symbols

10: Warping model

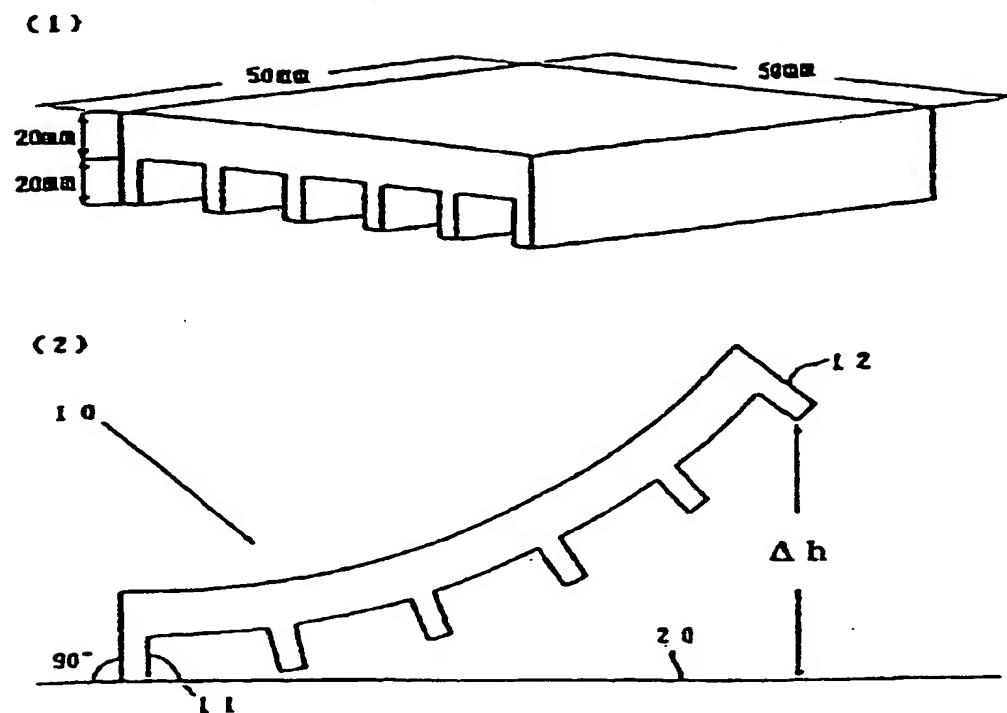
11, 12: Leg

20: Horizontal stand

5

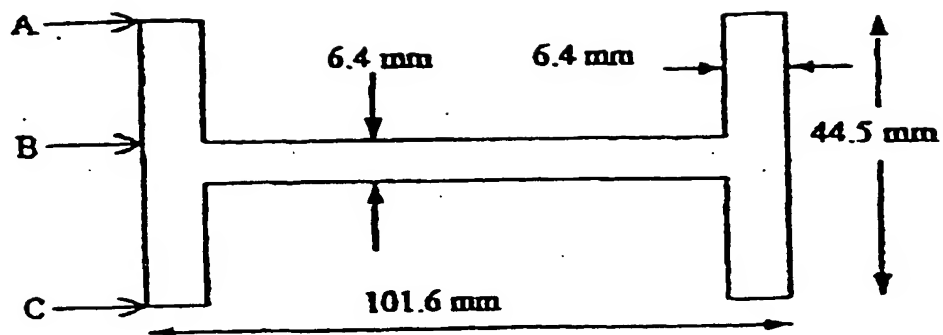
Drawing

[Fig. 1]





[Fig 2]



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/NL 00/00256

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G59/00 C08G65/18 G03C9/08 G03F7/027

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G G03C G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP 0 938 026 A (JSR CORP ; JAPAN FINE COATINGS CO LTD (JP); DSM NV (NL)) 25 August 1999 (1999-08-25) page 4, line 22 - page 5, line 21 page 8, line 50 - page 9, line 42	1, 3-9
X	EP 0 848 294 A (JAPAN SYNTHETIC RUBBER CO LTD ; JAPAN FINE COATINGS CO LTD (JP); DS) 17 June 1998 (1998-06-17) page 13, line 47 - line 50 claims 1, 2	1-9
X	EP 0 848 293 A (JAPAN SYNTHETIC RUBBER CO LTD ; JAPAN FINE COATINGS CO LTD (JP); DS) 17 June 1998 (1998-06-17) claim 1 page 19, line 5 - line 11	1, 3-9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

27 July 2000

Date of mailing of the international search report

04/08/2000

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# INTERNATIONAL SEARCH REPORT

Intern      ial Application No  
PCT/NL 00/00256

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 848 292 A (JAPAN SYNTHETIC RUBBER CO LTD ; JAPAN FINE COATINGS CO LTD (JP); DS) 17 June 1998 (1998-06-17) page 9, line 22 - line 28 claim 1 -----	1,3-9
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